Total Synthesis of Brasoside and Littoralisone

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Supporting Information

General Information. Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] CH_3CN was stored under argon over activated molecular sieves. TMSOTf was doubly distilled from CaH_2 prior to use. Non-aqueous reagents were transferred under argon via syringe or cannula. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel or Iatrobeads® according to the method of Still.[3] Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by fluorescence quenching or by anisaldehyde stain.

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 (300 MHz and 75 MHz) or 500 (500 MHz and 125 MHz) Spectrometer as noted, and are internally referenced to residual protio solvent signals. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Where appropriate, the notations H1, H2, H3, H4, H5, and H6 have been used to refer to protons residing on the denoted carbons in a sugar. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the California Institute of Technology Mass Spectral Facility. Optical rotations were measured on a Jasco P-1010 polarimeter, and $[\alpha]_D$ values are reported in 10^{-1} dg cm^2 g^{-1}.

(*S*)-3,7-dimethyloct-6-enyl 2,4,6-trimethylbenzoate. To a stirring solution of (–)-citronellol (8.8 mL, 48 mmol), pyridine (7.8 mL, 96 mmol), and DMAP (100 mg, 0.82 mmol) in CH_2Cl_2 (250 mL) was added 2,4,6-trimethylbenzoyl chloride (9.0 mL, 53 mmol). After 10 h the solution was diluted in 500 mL Et_2O and washed with 150 mL saturated solutions of NH_4Cl, $NaHCO_3$, and NaCl. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (95:5 pentane:Et_2O) afforded the title compound as a clear, colorless oil in 99% yield (14.4 g, 47.5 mmol). IR (film) 2956, 2921, 2852, 1778, 1726, 1613, 1453, 1436, 1376, 1264, 1214, 1170, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) □ 6.85 (s, 2H, Ar-**H**); 5.09 (m, 1H, $(CH_3)_2C=C\mathbf{H}$); 4.35 (m, 2H, $C\mathbf{H_2}OMes$); 2.29 (s, 9H, $ArC\mathbf{H_3}$); 1.96 (m, 2H, $C=CHC\mathbf{H_2}$); 1.82-1.26 (m, 11H, $C=C(C\mathbf{H_3})_2$, $C\mathbf{H_2}CHCH_3$, $C\mathbf{H}CH_3$); 1.02 (d, 3H, J = 6.6 Hz, $CHC\mathbf{H_3}$); ^{13}C NMR (75 MHz, $CDCl_3$) □ 170.5, 151.1, 139.3, 135.2, 131.6, 131.4, 128.9, 128.6, 124.9, 63.5, 40.6, 37.2, 35.9, 29.7, 25.9, 25.7, 21.2, 20.0, 19.5, 17.8; HRMS (FAB+) exact mass calculated for $[M + H]^+$ ($C_{20}H_{31}O_2$) requires m/z 303.2324, found m/z 303.2333. $[□]_D^{25}$ = –1.84 (c = 1.0, $CHCl_3$).

(*S*)-5-formyl-3-methylpentyl 2,4,6-trimethylbenzoate (7). A solution of (*S*)-3,7-dimethyloct-6-enyl 2,4,6-trimethylbenzoate (9.0 g, 30 mmol) and pyridine (2.6 mL, 45 mmol) in CH_2Cl_2/MeOH (140 mL/15 mL) was cooled to –78 °C. Ozone was bubbled through the solution until a dark blue color developed. At this time triphenylphosphine (8.6 g, 33 mmol) was added and the resulting mixture was stirred for 3 h allowing it to reach 0 °C. After concentration, flash chromatography (19:1-10:1 pentane:Et_2O) afforded the title compound as a clear, colorless oil in 96% yield (7.96 g, 28.8 mmol). IR (film) 2959, 2926, 2873, 1724, 1612, 1458, 1435, 1380, 1266, 1170, 1085, 958.7, 853.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) □ 9.77 (t, 1H, J = 1.8 Hz, $C\mathbf{H}O$); □ 6.85 (s, 2H, Ar-**H**); 4.36 (m, 2H, $C\mathbf{H_2}OMes$); 2.46 (m, 2H, $C\mathbf{H_2}CHO$); 2.28 (s, 9H, $ArC\mathbf{H_3}$); 1.83-1.46 (m, 5H, $C\mathbf{H_2}CHCH_3$, $C\mathbf{H}CH_3$); 0.96 (d, 3H, J = 6.3 Hz, $CHC\mathbf{H_3}$); ^{13}C NMR (75 MHz, $CDCl_3$) □ 202.4, 170.3, 151.1, 139.4, 135.1, 131.4, 128.6, 128.5, 63.1, 41.6, 35.6, 29.6, 28.9, 21.3, 20.0, 19.2, 19.1; HRMS (EI+) exact mass calculated for $[M]^+$ ($C_{17}H_{24}O_3$) requires m/z 276.1728, found m/z 276.1726. $[□]_D^{25}$ = –0.33 (c = 1.0, $CHCl_3$).

(*E*,3*R*,5*S*)-7-(methoxycarbonyl)-5-hydroxy-3-methylhept-6-enyl 2,4,6-trimethylbenzoate (8). D-Proline (530 mg, 4.6 mmol) was added to a stirring solution of **7** (3.12 g, 11.3 mmol) and nitrosobenzene (1.21 g, 11.3 mmol) in DMSO (45 mL). After 0.5 h the solution

became a bright orange, at which time it was cooled to –15 °C. A premixed solution of methyl diethyl phosphonoacetate (6.0 mL, 34 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (5.1 mL, 34 mmol) and lithium chloride (1.44 g, 34 mmol) in CH_3CN (45 mL) was added over 5 min via cannula. After 15 min the solution was diluted with MeOH (150 mL) and NH_4Cl (1.8 g, 34 mmol) was added. The resulting mixture was allowed to warm to room temperature and stand for 2 d. At this time the solution was diluted with Et_2O (700 mL), and washed successively with 200 mL saturated solutions of NH_4Cl, $NaHCO_3$, and NaCl. The aqueous layers were extracted with 3x100 mL CH_2Cl_2, and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (5:1-3:2 pentane:Et_2O) afforded the title compound as a clear, colorless oil in 56% yield (2.2 g, 6.33 mmol). IR (film) 3479, 2958, 2925, 1723, 1612, 1455, 1436, 1267, 1170, 1085, 1036, 983.8, 853.0 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) □ 6.95 (dd, 1H, *J* = 15.6, 4.8 Hz, C=C**H**CHOH); 6.85 (s, 2H, Ar-**H**); 6.05 (dd, 1H, *J* = 15.6, 1.6 Hz, C=C**H**CO_2Me); 4.45-4.27 (m, 3H, C**H**$_2$OMes, C**H**OH); 3.74 (s, 3H, OC**H**$_3$); 2.28 (s, 9H, ArC**H**$_3$); 1.98-1.24 (m, 5H, C**H**$_2$CHCH_3, C**H**CH_3); 1.01 (d, 3H, *J* = 6.6 Hz, CHC**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) □ 170.6, 167.3, 151.8, 139.4, 135.2, 135.0, 131.4, 128.6, 128.5, 119.4, 68.6, 63.2, 51.7, 43.8, 36.3, 26.6, 21.3, 20.0, 19.9 19.1; HRMS (EI+) exact mass calculated for [M + H]$^+$ ($C_{20}H_{29}O_5$) requires *m/z* 349.2015, found *m/z* 349.2023. $[\square]_D^{25}$ = –5.78 (c = 1.0, $CHCl_3$).

(*E*,3*R*,5*S*)-7-(methoxycarbonyl)-5-(*tert*-butyl-diphenyl-silanyloxy)-3-methylhept-6-enyl 2,4,6-trimethylbenzoate. *tert*-Butylchlorodiphenylsilane (4.6 mL, 17.8 mmol) was added to a stirring solution of **8** (3.1 g, 8.9 mmol), imidazole (1.5 g, 22.2 mmol), and DMAP (100 mg, 0.82 mmol) in DMF (20 mL). After 12 h the solution was diluted in 250 mL Et_2O and washed with 50 mL saturated solutions of NH_4Cl, $NaHCO_3$, and NaCl. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (85:15 pentane:Et_2O) afforded the title compound as a clear, colorless oil in 97% yield (5.1 g, 8.63 mmol). IR (film) 3072, 3049, 2957, 2931, 2858, 1726, 1612, 1472, 1428, 1362, 1267, 1170, 1112, 1085, 1036, 852.6, 821.8, 740.9, 702.0, 607.9, 504.3 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) □ 7.81-7.34 (m, 10H, SiPh**H**); 6.90 (dd, 1H, *J* = 15.6, 5.4 Hz, C=C**H**CHOSi); 6.87 (s, 2H, Ar-**H**); 5.86 (d, 1H, *J* = 15.6 Hz, C=C**H**CO_2Me); 4.39 (m, 1H, C**H**OSi); 4.20 (m, 2H, C**H**$_2$OMes); 3.72 (s, 3H, OC**H**$_3$); 2.29 (s, 9H, ArC**H**$_3$); 1.76-1.28 (m, 5H, C**H**$_2$CHCH_3, C**H**CH_3); 1.10 (s, 9H, SiC(C**H**$_3$)$_3$); 0.90 (d, 3H, *J* = 6.6 Hz, CHC**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) □ 170.5, 167.1, 150.6, 139.4, 136.2, 136.1, 136.0,

135.6, 135.5, 135.3, 135.1, 134.0, 130.5, 130.3, 130.1, 129.9, 128.6, 128.1, 128.0, 127.9, 127.8, 120.1, 71.3, 63.2, 51.8, 45.1, 35.8, 27.3, 26.8, 26.7, 26.4, 21.4, 20.0, 19.9, 19.6; HRMS (FAB+) exact mass calculated for $[M + H]^+$ ($C_{36}H_{47}O_5Si$) requires *m/z* 587.3193, found *m/z* 587.3192. $[\alpha]_D^{25} = -12.13$ (c = 1.0, $CHCl_3$).

(*E*,4*S*,6*R*)-6-methyl-4-(*tert*-butyl-diphenyl-silanyloxy)-oct-2-ene-1,8-diol. A 1M solution of diisobutylaluminum hydride in hexanes (75 mL, 75 mmol) was slowly added to a stirred –78 °C solution of (*E*,3*R*,5*S*)-7-(methoxycarbonyl)-5-(*tert*-butyl-diphenyl-silanyloxy)-3-methylhept-6-enyl 2,4,6-trimethylbenzoate (7.4 g, 12.6 mmol) in Et_2O (250 mL). After 30 min MeOH (3 mL) was slowly added, followed by dilution with 250 mL Et_2O and warming to room temperature. Saturated Rochelle's salt (300 mL) was then added, followed by vigorous stirring overnight. The aqueous layer was then separated and extracted with 2x100 mL CH_2Cl_2 and Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (1:3 pentane:Et_2O) afforded the title compound as a clear, colorless oil in 96% yield (5.0 g, 12.1 mmol). IR (film) 3338, 3072, 3049, 2956, 2930, 2858, 1472, 1462, 1428, 1362, 1112, 1057, 972.6, 822.2, 739.1, 702.2, 612.4, 504.8 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70-7.32 (m, 10H, SiPh**H**); 5.56 (ddt, 1H, *J* = 16.2, 7.5, 1.2 Hz, C=C**H**CH_2OH); 5.38 (ddt, 1H, *J* = 16.2, 5.5, 0.6 Hz, C=C**H**CHOSi); 4.24 (m, 1H, C**H**OSi); 3.87 (d, 2H, *J* = 5.5 Hz, CHC$\mathbf{H_2}$OH); 3.56 (m, 2H, $CH_2C\mathbf{H_2}$OH); 1.76-1.18 (m, 5H, C$\mathbf{H_2}$$CHCH_3$, C**H**$CH_3$); 1.06 (s, 9H, SiC(C$\mathbf{H_3}$)$_3$); 0.78 (d, 3H, *J* = 6.9 Hz, CHC$\mathbf{H_3}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.4, 136.2, 135.0, 134.8, 129.9, 129.8, 129.6, 129.5, 128.0, 127.9, 127.8, 127.6, 72.5, 63.2, 61.0, 45.6, 39.9, 27.4, 27.3, 27.2, 25.7, 20.3, 19.6; HRMS (FAB+) exact mass calculated for $[M + H]^+$ ($C_{25}H_{37}O_3Si$) requires *m/z* 413.2512, found *m/z* 413.2513. $[\alpha]_D^{25} = -19.57$ (c = 1.0, $CHCl_3$).

(1*S*,4a*R*,5*S*,7*S*,7a*R*)-1,4a,5,6,7,7a-hexahydro-5-(*tert*-butyl-diphenyl-silanyloxy)-7-methylcyclopenta[*c*]pyran-1-yl acetate (11). Dess-Martin periodinane (2.54 g, 6.1 mmol) was added to a stirred solution of (*E*,4*S*,6*R*)-6-methyl-4-(*tert*-butyl-diphenyl-silanyloxy)-oct-2-ene-1,8-diol (1.07 g, 2.60 mmol) in CH_2Cl_2 (26 mL). After 40 min the reaction was concentrated and extracted with 3x50 mL pentane. The combined organics were concentrated *in vacuo*, providing 1.0 g (94% yield, 2.44 mmol) of the corresponding dialdehyde, which was immediately redissolved in DMSO (61 mL). L-Proline (93 mg, 0.80 mmol) was added to this stirred solution

in one portion. After 5 h, the reaction was warmed to 40 °C and stirred at this temperature for 60 h at which point TLC analysis showed completion. The reaction was then cooled to 0 °C, and acetic anhydride (2.3 mL, 24 mmol) was added, followed by pyridine (1.0 mL, 12 mmol) and DMAP (25 mg, 0.23 mmol). After 15 min the reaction was diluted with 200 mL Et_2O and washed with 50 mL saturated solutions of NH_4Cl, $NaHCO_3$, and NaCl. The aqueous layers were then extracted with 2x50 mL CH_2Cl_2 and 2x50 mL Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (19:1 pentane:Et_2O) afforded the title compound as a clear, colorless oil in 83% yield (910 mg, 2.02 mmol). IR (film) 3072, 2956, 2931, 2858, 1761, 1652, 1472, 1428, 1362, 1211, 1112, 1026, 953.8, 702.3 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) □ 7.70-7.35 (m, 10H, SiPh**H**); 6.35 (dd, 1H, *J* = 6.3, 2.4 Hz, OC**H**=CH); 6.08 (d, 1H, *J* = 6.6, C**H**OAc); 5.05 (dd, 1H, *J* = 6.3, 2.7 Hz, OCH=C**H**); 4.32 (dd, 1H, *J* = 12.0, 6.6 Hz, C**H**OSi); 2.59 (m, 1H, C=CHC**H**); 2.10 (s, 3H, OC(O)C**H$_3$**); 2.08-1.84 (m, 3H, C**H**$_2$CHCH$_3$, C**H**CH$_3$, C**H**CHOAc); 1.24 (m, 1H, C**H**$_2$CHCH$_3$); 1.08 (s, 9H, SiC(C**H$_3$**)$_3$); 0.94 (d, 3H, *J* = 6.9 Hz, CHC**H$_3$**); ^{13}C NMR (75 MHz, $CDCl_3$) □ 170.0, 141.0, 136.1, 136.0, 135.9, 135.8, 130.0, 129.9, 129.8, 127.9, 127.8, 127.7, 101.3, 91.6, 75.3, 46.0, 40.9, 38.8, 31.6, 27.2, 21.5, 21.4, 19.5; HRMS (FAB+) exact mass calculated for $[M + H]^+$ ($C_{27}H_{35}O_4Si$) requires *m/z* 451.2305, found *m/z* 451.2305. $[\alpha]_D^{25} = -104.1$ (c = 1.0, $CHCl_3$).

(1*S*,4a*S*,5*S*,7*S*,7a*R*)-4-formyl-1,4a,5,6,7,7a-hexahydro-5-(*tert*-butyl-diphenyl-silanyloxy)-7-methylcyclopenta[*c*]pyran-1-yl acetate. DMF (6 mL) that had been stored over activated molecular sieves for at least 24 h was added to a flame-dried schlenk flask and cooled to –20 °C. Freshly distilled phosphorous oxychloride (0.84 mL, 9.0 mmol) was added dropwise with stirring. The mixture was allowed to slowly warm to room temperature over the course of 1 h, and then stirred at that temperature for an additional 1 h. A solution of **11** (580 mg, 1.3 mmol) in DMF (3 mL) was then added dropwise, and the resulting mixture was warmed to 40 °C. After 60 h the reaction was cooled to –20 °C, quenched by addition of 10 mL of a saturated solution of $NaHCO_3$, and extracted with 3x50 mL Et_2O. The combined organics were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (5:1 pentane:Et_2O) afforded the title compound as a clear, colorless oil in 73% yield (451 mg, 0.94 mmol). IR (film) 3072, 2957, 2931, 2858, 1766, 1677, 1633, 1472, 1428, 1367, 1215, 1183, 1091, 1071, 821.6, 740.0, 704.5 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) □ 9.18 (s, 1H, C**H**O); 7.67-7.29 (m, 11H, SiPh**H,** OC**H**=C);

6.45 (d, 1H, *J* = 9.3, C**H**OAc); 4.60 (apparent t, 1H, *J* = 3.4 Hz, C**H**OSi); 2.83 (dd, 1H, *J* = 8.8, 3.4, Hz C=CC**H**); 2.22 (s, 3H, OC(O)C**H$_3$**); 2.13 (m, 1H, C**H**CHOAc); 1.85-1.71 (m, 2H, C**H**-$_2$CHCH$_3$, C**H**CH$_3$); 1.20 (m, 1H, C**H$_2$**CHCH$_3$); 1.02 (s, 12H, SiC(C**H$_3$)$_3$**, CHC**H$_3$**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.0, 169.7, 162.7, 136.4, 136.3, 136.2, 136.1, 134.2, 133.2, 129.9, 129.8, 127.8, 127.7, 127.6, 119.1, 96.3, 76.1, 44.7, 43.5, 40.2, 34.2, 27.3, 27.2, 21.7, 21.2, 19.6; HRMS (FAB+) exact mass calculated for $[M + H]^+$ ($C_{28}H_{35}O_5Si$) requires *m/z* 479.2254, found *m/z* 479.2266. $[\alpha]_D^{25}$ = –13.82 (c = 1.0, $CHCl_3$).

(1*S*,4a*S*,5*S*,7*S*,7a*R*)-1-acetoxy-1,4a,5,6,7,7a-hexahydro-5-(*tert*-butyl-diphenyl-silanyloxy)-7-methylcyclopenta[*c*]pyran-4-carboxylic acid. Sodium hypochlorite (1.06 g, 9.4 mmol) was added to a stirred solution of NaH_2PO_4 (864 mg, 6.3 mmol) in H_2O (3.2 mL). The resulting solution was added dropwise over 30 min to a stirred mixture of (1*S*,4a*S*,5*S*,7*S*,7a*R*)-4-formyl-1,4a,5,6,7,7a-hexahydro-5-(*tert*-butyl-diphenyl-silanyloxy)-7-methylcyclopenta[*c*]pyran-1-yl acetate (300 mg, 0.63 mmol) in 2-methyl butene (4.2 mL) and tBuOH (6.3 mL). The resulting solution was stirred for 24 h, at which time an additional portion of sodium hypochlorite (354 mg, 3.1 mmol) and NaH_2PO_4 (288 mg, 2.1 mmol) in H_2O (1.0 mL) was added. After a further 24 h of stirring, the reaction was diluted with 10 mL H_2O, and extracted with 3x20 mL CH_2Cl_2 and 3x20 mL Et_2O. The combined organics were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (5:1-1:6 pentane:Et_2O) afforded the title compound as a clear, colorless oil in 93% yield (288 mg, 0.58 mmol). IR (film) 3073, 2958, 2932, 2859, 1764, 1682, 1634, 1428, 1367, 1287, 1193, 1089, 960.2, 912.0, 737.0, 704.3 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (s, 1H, OC**H**=C); 7.69-7.29 (m, 10H, SiPh**H**); 6.40 (d, 1H, *J* = 8.7 Hz, C**H**OAc); 4.52 (m, 1H, C**H**OSi); 2.77 (dd, 1H, *J* = 8.4, 3.0 Hz, C=CC**H**); 2.22 (s, 3H, OCOC**H$_3$**); 2.15 (m, 1H, C**H**CHOAc); 1.86-1.73 (m, 2H, C**H$_2$**CHCH$_3$, C**H**CH$_3$); 1.24 (m, 1H, C**H$_2$**CHCH$_3$); 1.04 (s, 12H, SiC(C**H$_3$)$_3$**, CHC**H$_3$**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 169.9, 156.2, 136.4, 136.3, 136.2, 136.1, 134.5, 133.1, 129.9, 129.8, 127.8, 127.7, 127.6, 105.7, 95.5, 76.4, 44.9, 43.1, 42.3, 34.2, 27.3, 27.2, 21.7, 21.2, 19.4; HRMS (FAB+) exact mass calculated for $[M + H]^+$ ($C_{28}H_{35}O_6Si$) requires *m/z* 495.2203, found *m/z* 495.2225. $[\alpha]_D^{25}$ = –13.82 (c = 1.0, $CHCl_3$).

Iridolactone (4). A solution of HF•pyridine (2 mL, 70% HF) was added to a stirred solution of (1*S*,4a*S*,5*S*,7*S*,7a*R*)-1-acetoxy-1,4a,5,6,7,7a-hexahydro-5-(*tert*-butyl-diphenyl-silanyloxy)-7-methylcyclopenta[*c*]pyran-4-carboxylic acid (240 mg, 0.48 mmol) in THF (4 mL). After 10 h the reaction was diluted with 50 mL Et_2O, and washed with 20 mL of a saturated $NaHCO_3$ solution (Caution: violent bubbling). The aqueous layer was thoroughly extracted with 3x20 mL CH_2Cl_2 and Et_2O. The combined organics were dried over Na_2SO_4 and concentrated *in vacuo*. The resultant residue was then immediately dissolved in CH_2Cl_2 (10 mL), at which time 1,3-dicyclohexyl carbodiimide (150 mg, 0.73 mmol) was added in one portion. After 15 min, the reaction was concentrated *in vacuo*. Flash chromatography (5:1-1:4 pentane:Et_2O) afforded the title compound as a clear, colorless oil in 82% yield (95 mg, 0.40 mmol). IR (film) 2954, 2931, 2854, 1756, 1661, 1237, 1216, 1170, 1012, 972.2, 872.0 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) □ 7.31 (d, 1H, 2.7 Hz, OC**H**=C); 6.35 (s, 1H, C**H**OAc); 5.06 (apparent t, 1H, *J* = 4.6 Hz, C**H**OC(O)); 3.42 (m, 1H, C=CC**H**); 2.20-2.10 (m, 4H, OCOC**H$_3$**, C**H**CHOAc); 1.98 (m, 1H, C**H$_2$**CHCH$_3$); 1.66 (m, 1H, C**H**CH$_3$); 1.24 (m, 1H, C**H$_2$**CHCH$_3$); 1.07 (d, 3H, *J* = 6.3 Hz, CHC**H$_3$**); ^{13}C NMR (75 MHz, $CDCl_3$) □ 170.2, 169.2, 148.3, 103.6, 88.8, 81.1, 45.0, 42.0, 38.1, 31.8, 20.9, 17.6; HRMS (EI+) exact mass calculated for $[M]^+$ ($C_{12}H_{14}O_5$) requires *m/z* 238.0841, found *m/z* 238.0838. $[\alpha]_D^{25}$ = –229.2 (c = 1.0, $CHCl_3$).

Brasoside Tetraacetate. 1-*O*-(Trimethylsilyl)-2,3,4,6-tetra-*O*-acetyl-□-D-glucopyranose (31.5 mg, 0.075 mmol, prepared according to the method of Allevi[4]) and **4** (7.0 mg, 0.030 mmol) were added as benzene solutions to a schlenk flask under argon. The benzene was then frozen and sublimed. The remaining solid was redissolved in CH_3CN (0.15 mL) and cooled to – 30 °C. At this time TMSOTf (2.3 □L, 0.012 mmol) was added dropwise as a 5% solution in CH_3CN. After stirring at –30 °C for 3 d, the reaction was quenched with 1 mL pH 7 buffer and extracted with 3x10 mL Et_2O. The combined organics were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (1:1-1:3 pentane:Et_2O) afforded the title compound as a clear, colorless oil in 86% yield (13.6 mg, 0.026 mmol). The spectral data (^1H and ^{13}C) were in full accord with those reported for the natural isolate,[5,6] except for the IR and HRMS which have not been described: IR (film) 2955, 2920, 2858, 1756, 1660, 1367, 1219, 1216, 1038, 1013, 972.8, 862.2cm^{-1}; HRMS (EI+) exact mass calculated for $[M + H]^+$ ($C_{24}H_{31}O_{13}$) requires *m/z* 527.1765, found *m/z* 527.1764. $[\alpha]_D^{25}$ = –270.9 (c = 1.0, $CHCl_3$); lit: $[\alpha]_D$ = –229 (c = 0.9, $CHCl_3$).[5]

Brasoside (2). A solution of MeOH:Et_3N:H_2O (0.08 mL, 8:1:1) was added slowly to a –15 °C solution of Brasoside tetraacetate (5.0 mg, 0.007 mmol) in CH_2Cl_2 (0.04 mL). After 3 h the reaction was quenched with 0.5 mL pH 7 buffer, and extracted with 3x5 mL EtOAc. The combined organics were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (9:1 EtOAc:MeOH) afforded the title compound as a white powder in 90% yield (2.3 mg, 0.0063 mmol). The spectral data (^{1}H and ^{13}C) were in full accord with those already reported (Table 2),[5-7] except for the IR and HRMS which have not been described: IR (film) 2960, 2917, 2849, 1749, 1654, 1261, 1090, 1019, 799.0 cm^{-1}; HRMS (FAB+) exact mass calculated for $[M + H]^+$ ($C_{16}H_{23}O_9$) requires *m/z* 359.1342, found *m/z* 359.1332. $[\alpha]_D^{25}$ = –181.0 (c = 0.41, EtOH); lit: $[\alpha]_D$ = –170 (c = 0.97, EtOH)[5]; $[\alpha]_D$ = –283 (c = 1.4, EtOH)[6].

(*E*)-2-hydroxyethyl 3-(4-(benzyloxy)phenyl)acrylate. Oxalyl chloride (8 mL, 2M solution in CH_2Cl_2) was added to a stirred solution of *p*-benzyloxycinammic acid (2.89 g, 11.3 mmol, prepared according to the method of Doherty[8]) in CH_2Cl_2 (45 mL) at 0 °C. A few drops of DMF were then added, and the resulting solution was stirred at 0°C for 1 h and at 23 °C for a further 1 h. At this stage the solution was added dropwise via cannula to a stirred mixture of ethylene glycol (12.6 mL, 226 mmol), triethylamine (4 mL, 28 mmol), and DMAP (100 mg, 0.82 mmol) in CH_2Cl_2 (110 mL) cooled to 0 °C. The resulting solution was stirred for 12 h, at which time the reaction was quenched with a saturated solution of $NaHCO_3$ (200 mL), and after extraction the organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (4:1 Et_2O:pentane) afforded the title compound as a white solid in 93% yield (3.14 g, 10.5 mmol). IR (film) 3420, 2956, 2932, 2859, 1707, 1636, 1602, 1511, 1254, 1172, 984.1, 825.5 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, 1H, *J* = 16.2 Hz, ArC**H**=CH); 7.50-7.35 (m, 7H, Ar**H**); 6.98 (d, 2H, *J* = 9.0 Hz, Ar**H**); 6.34 (d, 1H, *J* = 16.2 Hz, ArCH=C**H**); 5.10 (s, 2H, C**H$_2$**Ph); 4.35 (m, 2H, CO_2C**H$_2$**CH_2); 3.90 (dd, 2H, *J* = 9.0, 5.1 Hz, CO_2CH_2C**H$_2$**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 160.9, 145.3, 136.7, 130.2, 128.9, 128.4, 127.7, 127.4, 115.5, 115.4, 70.3, 66.4, 61.5; HRMS (FAB+) exact mass calculated for $[M + H]^+$ ($C_{18}H_{19}O_4$) requires *m/z* 299.1283, found *m/z* 299.1276.

Enolsilane (13). Dess-Martin periodinane (2.15 g, 5.1 mmol) was added to a stirred solution of (*E*)-2-hydroxyethyl 3-(4-(benzyloxy)phenyl)acrylate (1.21 g, 4.06 mmol) in CH_2Cl_2

(20 mL). After 10 h the reaction was concentrated and extracted with 3x50 mL Et_2O. The combined organics were concentrated *in vacuo*, providing 1.15 g (95% yield, 5.8 mmol) of the corresponding aldehyde, which was immediately redissolved in CH_3CN (5 mL). The resulting solution was added dropwise to a premixed solution of triethylamine (3.75 mL, 27 mmol) and chlorotrimethylsilane (2.44 mL, 19.2 mmol) in CH_3CN (5 mL). This mixture was stirred for 2 h, at which time the reaction was concentrated *in vacuo*. Flash chromatography (3:1 pentane:Et_2O) on Iatrobeads afforded the title compound as a white solid in 82% yield (1.75 g, 4.8 mmol). IR (film) 3117, 3065, 3035, 2958, 2931, 2898, 2860, 1732, 1682, 1634, 1601, 1511, 1270, 1158, 1122, 985.2, 843.5 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, 1H, *J* = 16.2 Hz, ArC**H**=CH); 7.51-7.36 (m, 7H, Ar**H**); 6.98 (d, 2H, *J* = 8.7 Hz, Ar**H**); 6.74 (d, 1H, *J* = 3.6 Hz, C**H**=CHOTMS); 6.39 (d, 1H, *J* = 16.2 Hz, ArCH=C**H**); 5.84 (d, 1H, *J* = 3.6 Hz, CH=C**H**OTMS); 5.10 (s, 2H, C$\mathbf{H_2}$Ph); 0.25 (s, 9H, Si(C$\mathbf{H_3}$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 161.0, 146.1, 136.6, 130.2, 130.0, 128.9, 128.4, 127.7, 127.4, 121.2, 115.5, 114.7, 70.3, -0.2; HRMS (FAB+) exact mass calculated for $[M + H]^+$ ($C_{21}H_{25}O_4Si$) requires *m/z* 369.1522, found *m/z* 369.1517.

2-*O*-Benzylcoumaroyl-4,6-bis-*O*-benzyloxy-α-D-glucopyranose (14). (2*R*,3*R*)-3-Hydroxy-2,3-bis-(benzylyloxy)-propionaldehyde (**12**) (125 mg, 0.42 mmol, prepared according to the method of MacMillan[9] using D-proline) was added as a solution in 2.0 mL of toluene to a flame-dried schlenk flask charged with finely divided magnesium bromide diethyl etherate (322 mg, 1.25 mmol, freshly prepared from magnesium turnings and dibromoethane in Et_2O) and 2.0 mL of toluene cooled to –20 °C. After stirring for 30 minutes at –20 °C, **13** (230 mg, 0.63 mmol) was added as a solution in 0.5 mL toluene. The suspension was stirred at –20 °C for 2 hours, then allowed to warm to 4 °C over the course of 4 hours. After stirring for an additional 24 hours at 4 °C, the reaction was acidified by the addition of 50 mL saturated aqueous NH_4Cl and extracted with Et_2O (3x50 mL). The combined organics were washed with 50 mL brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was taken up in 5 mL of 7:2:1 THF:water:trifluoroacetic acid at 0 °C and stirred for 30 minutes before being quenched with 50 mL 10% $NaHCO_3$, extracted with 2x100 mL Et_2O, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Crude ^1H NMR analysis indicated an 10:1 mixture of glucose:mannose derived diastereomers. Flash chromatography (1:1-4:1 Et_2O:pentane) afforded

the title compound as a white solid (163 mg, 0.27 mmol) in 65% yield, 8:1 □:□. IR (film) 3425, 3064, 3032, 2924, 2869, 1710, 1633, 1603, 1511, 1454, 1251, 1171, 1058, 910.58, 828.2, 743.8, 697.6 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) □-isomer: □ 7.72 (d, 1H, *J* = 15.9 Hz, ArC**H**=CH); 7.47-7.20 (m, 17H, Ar**H**); 6.94 (d, 2H, *J* = 8.7 Hz, Ar**H**); 6.37 (d, 1H, *J* = 15.9 Hz, ArCH=C**H**); 5.48 (m, 1H, H1); 5.06 (m, 2H, C**H**$_2$Ph); 4.87 (dd, 1H, *J* = 10.2, 3.9 Hz, H2); 4.85 (d, 1H, *J* = 11.4 Hz, C**H**$_2$Ph); 4.64-4.50 (m, 3H, C**H**$_2$Ph); 4.24 (m, 1H, H6); 4.09 (m, 1H, H6); 3.72-3.53 (m, 3H, H3, H4, H5); ^{13}C NMR (75 MHz, $CDCl_3$) □-isomer: □ 167.4, 161.0, 146.0, 138.4, 138.0, 136.6, 130.2, 128.9, 128.8, 128.7, 128.4, 128.3, 128.2, 128.0, 127.7, 127.4, 115.4, 114.9, 90.7, 78.5, 75.0, 74.0, 73.7, 72.0, 70.3, 70.0, 68.9; HRMS (FAB+) exact mass calcd for $[M+H]^+$ ($C_{36}H_{37}O_8$) requires *m/z* 597.2488, found *m/z* 597.2512; $[□]_D^{25}$ = 30.59 (c = 1.0, $CHCl_3$, 8:1 □:□ mixture).

2-*O*-Benzylcoumaroyl-3,4,6-tris-*O*-benzyloxy-□-D-glucopyranose. Benzyl bromide (0.132 mL, 1.1 mmol) was added to a solution of freshly prepared Ag_2O (255 mg, 1.1 mmol) and **12** (131 mg, 0.22 mmol) in 2.3 mL of CH_2Cl_2 stirred in the dark. After stirring for 18 h, the reaction was filtered through a pad of celite and concentrated *in vacuo*. The resulting residue was redissolved in MeOH (3 mL), at which time ammonium formate (208 mg, 3.3 mmol) and 10% Pd on alumina (220 mg) were added. The suspension was stirred for 10 hours, then filtered and concentrated *in vacuo*. Flash chromatography (1:1-3:1 Et_2O:pentane) afforded the title compound as a white solid (103 mg, 0.15 mmol) in 68% yield, 12:1 □:□. IR (film) 3424, 3063, 3030, 2892, 2868, 1713, 1631, 1602, 1510, 1453, 1249, 1172, 1060, 827.6, 736.4, 697.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) □-isomer: □ 7.70 (d, 1H, *J* = 15.9 Hz, ArC**H**=CH); 7.48-7.18 (m, 22H, Ar**H**); 6.98 (d, 2H, *J* = 8.7 Hz, Ar**H**); 6.33 (d, 1H, *J* = 15.9 Hz, ArCH=C**H**); 5.50 (t, 1H, *J* = 3.6 Hz, H1); 5.08 (m, 2H, C**H**$_2$Ph); 4.88-4.83 (m, 3H, H2, C**H**$_2$Ph); 4.64-4.51 (m, 4H, C**H**$_2$Ph); 4.21-4.14 (m, 2H, H6); 3.86 (m, 1H, H3); 3.72-3.67 (m, 2H, H4, H5); ^{13}C NMR (75 MHz, $CDCl_3$) □-isomer: □ 166.8, 161.0, 145.7, 138.7, 138.3, 138.0, 136.7, 130.2, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 115.5, 115.2, 90.9, 80.2, 78.4, 77.8, 77.4, 76.9, 75.8, 75.4, 73.9, 73.7, 70.5, 70.3, 69.0; HRMS (EI+) exact mass calcd for $[M]^+$ ($C_{43}H_{42}O_8$) requires *m/z* 686.2880, found *m/z* 686.2891; $[□]_D^{25}$ = 38.62 (c = 1.0, $CHCl_3$, 12:1 □:□ mixture).

1-*O*-(Trimethylsilyl)-2-*O*-Benzylcoumaroyl-3,4,6-tris-*O*-benzyloxy-β-D-glucopyranose (15). Chlorotrimethylsilane (27.8 μL, 0.22 mmol) was added dropwise over 20 min as a benzene (1 mL) solution to a refluxing mixture of triethylamine (0.202 mL, 1.46 mmol) and 2-*O*-benzylcoumaroyl-3,4,6-tris-*O*-benzyloxy-β-D-glucopyranose (100 mg, 0.146 mmol) in benzene (2.9 mL). After refluxing for 2 h, the reaction was filtered through a pad of celite and concentrated *in vacuo*. Flash chromatography (3:1 pentane: Et_2O) on Iatrobeads afforded the title compound as a clear oil that solidifies to a white solid on standing *in vacuo* (101 mg, 0.133 mmol) in 91% yield. IR (film) 3064, 3032, 2958, 2868, 1716, 1634, 1603, 1511, 1454, 1251, 1150, 1068, 846.6, 736.6, 697.3 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, 1H, *J* = 15.9 Hz, ArC**H**=CH); 7.55-7.25 (m, 22H, Ar**H**); 7.03 (d, 2H, *J* = 8.7 Hz, Ar**H**); 6.33 (d, 1H, *J* = 15.9 Hz, ArCH=C**H**); 5.20-5.15 (m, 3H, H1, C**H**$_2$Ph); 4.92-4.61 (m, 7H, H2, C**H**$_2$Ph); 3.85-3.76 (m, 4H, H3, H5, H6); 3.62 (m, 1H, H4); 0.24 (s, 9H, Si(C**H**$_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1, 160.9, 145.1, 138.6, 138.6, 138.4, 138.3, 136.8, 130.1, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 115.8, 115.6, 96.3, 83.0, 78.4, 75.7, 75.4, 75.3, 75.2, 73.8, 70.4, 69.3, 0.48; HRMS (FAB+) exact mass calcd for $[M - H]^+$ ($C_{46}H_{49}O_8Si$) requires *m/z* 757.3197, found *m/z* 757.3174; $[\alpha]_D^{25} = 44.67$ (c = 1.0, $CHCl_3$).

2-*O*-Benzylcoumaroyl-3,4,6-tris-*O*-benzyloxy-brasoside (16). 15 (71 mg, 0.094 mmol) and **4** (15 mg, 0.063 mmol) were added as benzene solutions to a schlenk flask under argon. The benzene was then frozen and evaporated. The remaining solid was redissolved in CH_3CN (0.25 mL) and cooled to –30 °C. At this time TMSOTf (6.1 μL, 0.031 mmol) was added dropwise as a 10% solution in CH_3CN. After 5 d stirring at –30 °C the reaction was quenched with 2 mL pH 7 buffer, and extracted with 3x15 mL Et_2O. The combined organics were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (50:1-25:1 CH_2Cl_2:Et_2O) afforded the title compound as a clear, colorless oil in 74% yield (40 mg, 0.047 mmol). IR (film) 3069, 3032, 2962, 2873, 1756, 1716, 1660, 1603, 1511, 1455, 1258, 1081, 800.0, 737.4, 698.4 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, 1H, *J* = 15.9 Hz, ArC**H**=CH); 7.49-7.15 (m, 23H, Ar**H**, OC**H**=C); 6.98 (d, 2H, *J* = 8.7 Hz, Ar**H**); 6.14 (d, 1H, *J* = 15.9 Hz, ArCH=C**H**); 5.52 (d, 1H, *J* = 0.9 Hz, OC**H**O-Glucose); 5.12-4.53 (m, 11H, H1, H2, C**H**$_2$Ph, C**H**OC(O)); 3.81-3.72 (m, 4H, H3, H5, H6); 3.58 (m, 1H, H4), 3.42 (dt, 1H, *J* = 6.9, 2.7 Hz, OC=CC**H**); 2.05 (m, 2H, C**H**$_2$CHCH$_3$, C**H**CHO-Glucose); 1.86 (m, 1H, C**H**CH$_3$); 1.54 (m, 1H, C**H**$_2$CHCH$_3$); 1.00 (d, 3H, *J* = 6.3 Hz,

CHC**H$_3$**); ^{13}C NMR (75 MHz, $CDCl_3$): □ 170.4, 165.9, 160.8, 147.7, 145.5, 137.8, 136.5, 133.8, 130.0, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.1, 115.3, 114.8, 106.7, 104.0, 96.3, 92.9, 82.5, 81.0, 77.7, 77.2, 75.4, 75.2, 75.1, 73.5, 72.7, 70.1, 68.4, 45.1, 42.1, 38.1, 31.4, 17.8; HRMS (FAB+) exact mass calcd for $[M + H]^+$ ($C_{53}H_{53}O_{11}$) requires *m/z* 865.3588, found *m/z* 865.3563; $[\alpha]_D^{25} = -37.42$ (c = 1.0, $CHCl_3$).

Littoralisone (1). **16** (10 mg, 0.012 mmol) was dissolved in degassed benzene (3.8 mL) in a Pyrex flask under argon. This solution was exposed to 350 nm UV light (Hitachi UVA lamps, Luzchem 10 lamp photoreactor) with stirring for 2 h. At this time the reaction was concentrated *in vacuo*, then redissolved in EtOAc/MeOH (2:1), and 10% Pd/C (5 mg) was added with stirring. This suspension was degassed and backfilled with H_2 three times, at which point it was kept under a slight positive pressure of H_2. After 30 min, the reaction was filtered, and concentrated *in vacuo*. Flash chromatography (50:1-25:1 CH_2Cl_2:MeOH) afforded the title compound as a white powder in 84% yield (5.1 mg, 0.010 mmol). ^{1}H and ^{13}C NMR, IR and HRMS spectra confirm that synthetic and natural **1** are identical in all respects (Table 1). IR (film) 3391, 1745, 1635, 1518, 1448, 1187, 1076, 972.4 cm^{-1}. Synthetic **1** $[\alpha]_D^{25} = -46.1$ (*c* = 0.4, MeOH), natural **1** $[\alpha]_D^{25} = -49.5$ (*c* = 0.4, MeOH)[10]. HRMS (FAB+) exact mass calcd for $[M + H]^+$ ($C_{25}H_{29}O_{11}$) requires *m/z* 505.1710, found *m/z* 505.1699.

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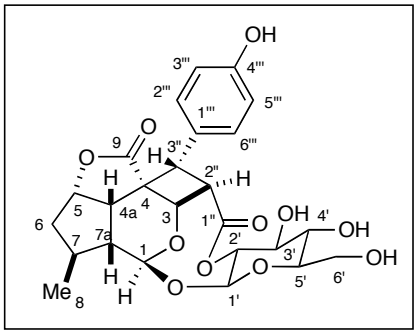
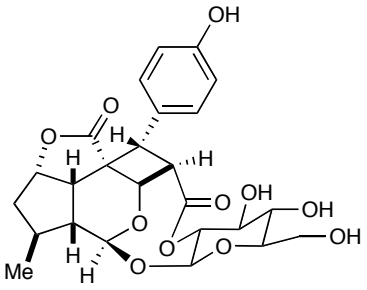


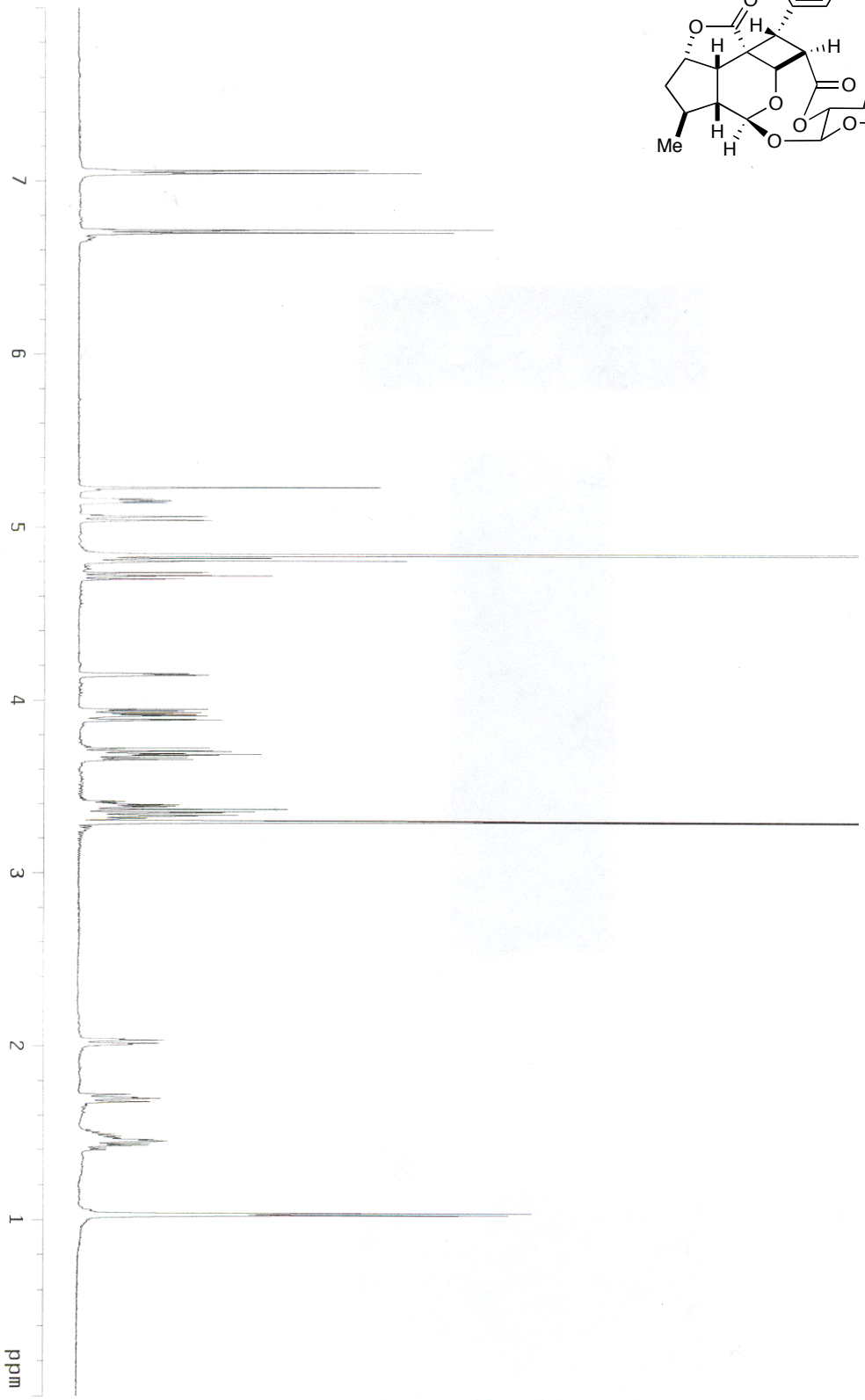
Table 1. ^{1}H and ^{13}C NMR Data for Natural[10] and Synthetic 1[a]

position	Natural Littoralisone[b]		Synthetic Littoralisone[c]	
	^{13}C (□)	^{1}H (□), m, J (Hz)	^{13}C (□)	^{1}H (□), m, J (Hz)
1	96.45	5.23, s	96.46	5.23, s
3	66.84	5.06, d, 11.1	66.87	5.04, d, 10.8
4	48.13		48.15	
4a	43.87	3.35, dd, 9.2, 4.6	43.90	3.33, dd, 9.0, 4.5
5	83.47	5.16, dd, 5.0, 4.6	83.48	5.15, dd, 6.8, 4.4
6	43.23	2.03 (H-6□), dd, 12.6, 3.8 1.42 (H-6□), dd, 12.6, 5.0	43.26	2.02 (H-6□), dd, 12.6, 3.9 1.41 (H-6□), dd, 12.6, 5.3
7	33.21	1.49, m	33.24	1.47, m
7a	46.98	1.70, dd, 11.8, 9.2	47.01	1.70, dd, 12.2, 9.0
8	16.58	1.03, d, 5.7	16.61	1.03, d, 5.7
9	176.94		176.96	
1’	100.37	4.83, d, 8.4	100.39	4.81, d, 8.3
2’	80.49	4.73, dd, 9.9, 8.4	80.51	4.72, dd, 9.8, 8.4
3’	74.59	3.72, dd, 9.9, 8.4	74.62	3.70, dd, 9.8, 8.4
4’	71.93	3.37, dd, 9.9, 8.4	71.94	3.36, dd, 9.8, 8.4
5’	79.54	3.41, ddd, 9.9, 5.3, 2.3	79.57	3.40, ddd, 9.8, 5.3, 2.0
6’	62.63	3.68 (H-6’a), dd, 11.8, 5.3 3.90 (H-6’b), dd, 11.8, 2.3	62.66	3.67 (H-6’a), dd, 12.2, 5.3 3.89 (H-6’b), dd, 12.2, 2.0
1”	175.13		175.14	0.97, d, 6.6
2”	50.14	3.94, dd, 11.1, 4.6	50.17	3.93, dd, 11.0, 4.6
3”	49.65	4.15, d, 4.6	49.66	4.14, d, 4.4
1”’	128.37		128.39	
2”’	130.32	7.06, dd, 6.5, 1.9	130.35	7.05, dd, 6.8, 1.9
3”’	116.19	6.72, dd, 6.5, 1.9	116.20	6.71, dd, 6.8, 1.9
4”’	157.79		157.84	
5”’	116.19	6.72, dd, 6.5, 1.9	116.20	6.71, dd, 6.8, 1.9
6”’	130.32	7.06, dd, 6.5, 1.9	130.35	7.05, dd, 6.8, 1.9

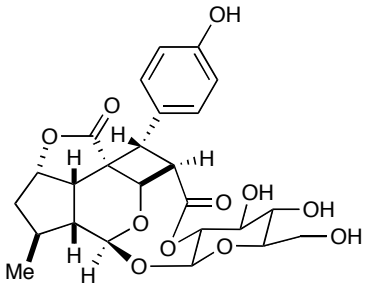
[a]Spectra were measured in CD_3OD. [b]^{1}H NMR (500 MHz); ^{13}C (125 MHz). [c]^{1}H NMR (500 MHz); ^{13}C (125 MHz).

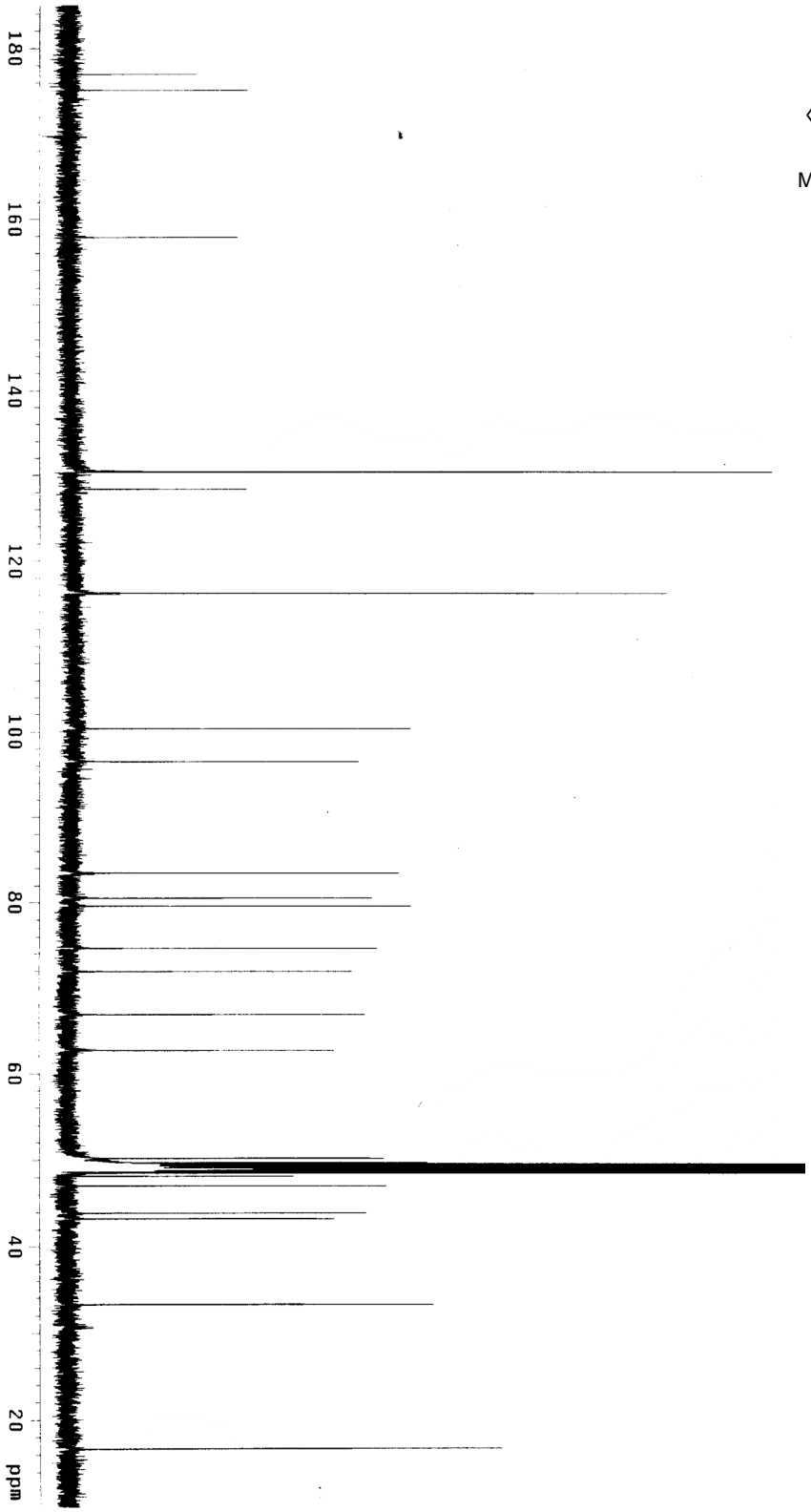
^{1}H NMR of synthetic **1**





^{13}C NMR of synthetic **1**





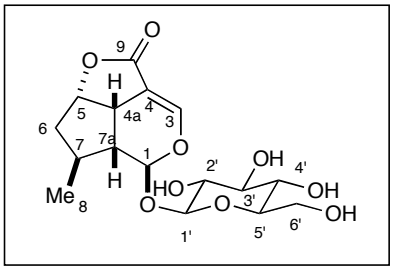
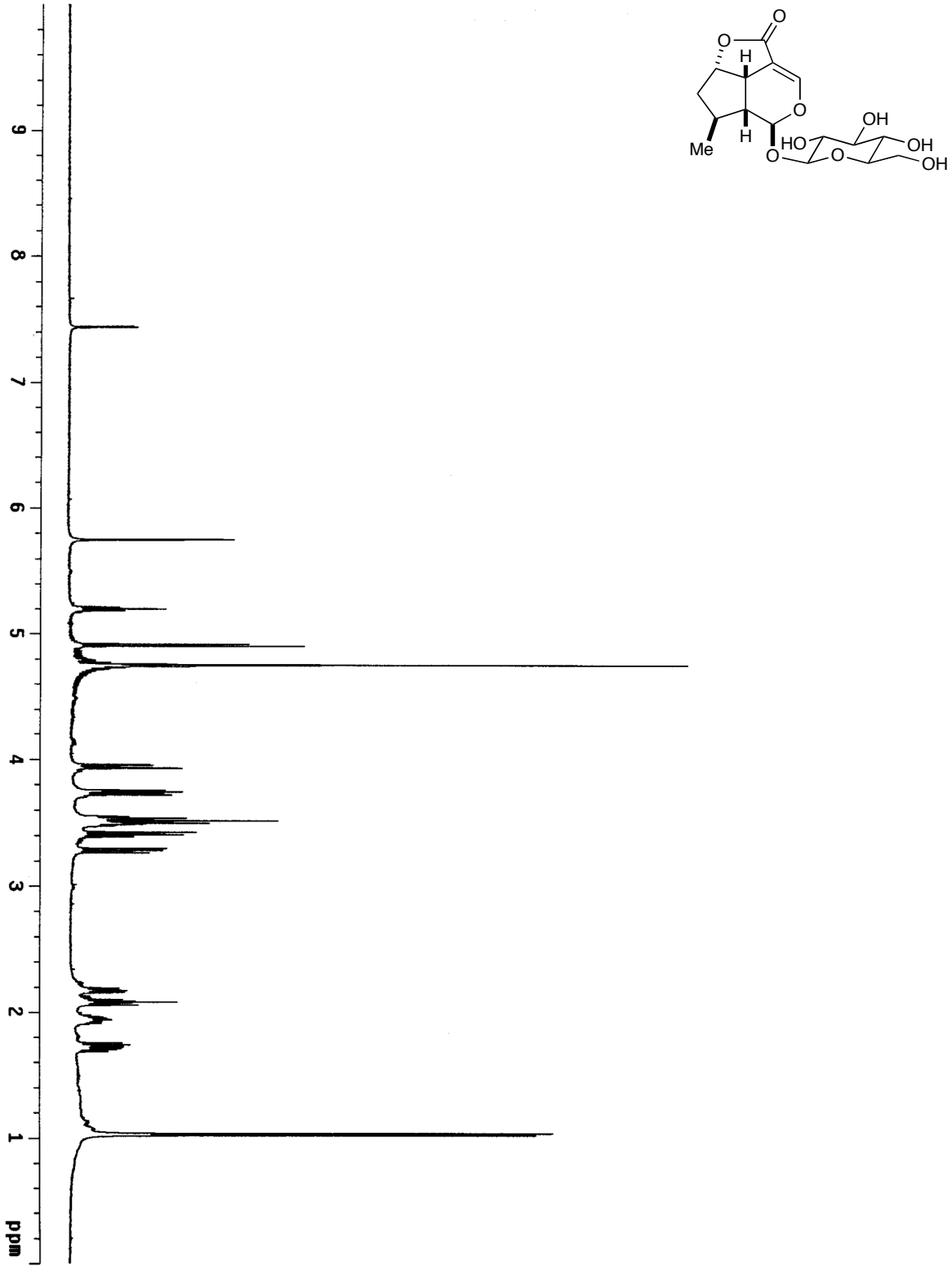


Table 1. ^{1}H and ^{13}C NMR Data for Natural[5] and Synthetic 2[a]

position	Natural Brasoside[b]		Synthetic Brasoside[c]	
	^{13}C (δ)	^{1}H (δ), m, J (Hz)	^{13}C (δ)	^{1}H (δ), m, J (Hz)
1	95.3	5.75, s	95.5	5.75, s
3	150.7	7.45, d, 2.6	150.8	7.44, d, 2.5
4	104.1		104.2	
4a	38.6	3.50, dt, 7.2, 2.5	38.7	3.49, m
5	84.4	5.20, t, 7.7	84.6	5.20, t, 7.5
6	41.8	2.08 (H-6α), dd, 15.2, 7.6 1.73 (H-6β), ddd, 15.1, 11.4, 8.0	41.8	2.07 (H-6α), dd, 15.0, 8.0 1.71 (H-6β), ddd, 15.0, 11.5, 8.0
7	32.3	1.94, m	32.3	1.93, m
7a	45.5	2.18, ddd, 11.0, 6.8, 0.8	45.6	2.16, ddd, 11.0, 6.5, 0.7
8	17.5	1.03, d, 7.0	17.5	1.02, d, 6.5
9	175.0		175.2	
1’	99.4	4.91, d, 8.0	99.5	4.90, d, 8.0
2’	73.4	--	73.4	3.30, dd, 9.3, 8.2
3’	76.3	--	76.3	3.55-3.47, m
4’	70.4	--	70.4	3.41, dd, 10.0, 9.3
5’	77.1	--	77.2	3.55-3.47, m
6’	61.5	--	61.5	3.74 (H-6’a), dd, 12.4, 5.0 3.94 (H-6’b), dd, 12.4, 2.2

[a]Spectra were measured in D_2O. [b]^{1}H NMR (500 MHz); ^{13}C (125 MHz). [c]^{1}H NMR (500 MHz); ^{13}C (125 MHz).

^{1}H NMR of synthetic **2**



^{13}C NMR of synthetic **2**